Evaluation of compatibility between sugarcane straw particles and Portland cement

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Abstract. Brazilian agro industries generate several types of crop residues and most of them show interesting properties for cement composite production. Among these residues, actually sugarcane straw particles (SCSP) are available in a great amount as a by-product of the sugarcane industries. However, residual sugar and other chemical products remain in the material's structure. In the most of the cases, these compounds inhibit cement setting. The aim of this research work was to evaluate, by means the hydration curve methodology, the performance of several treatments applied to the SCSP. Results indicated that mineralization was the most effective treatment and allows appropriate cement setting for the composite. SCSP treated by soaking in sodium silicate solution at 4%, followed by a second soaking in aluminum sulfate at 10%, showed an appropriate cement setting.

Keywords: cement composite, hydration curve, chemical treatment, mineralization, agricultural waste

Introduction

Brazil has one of the largest global agricultural productions in the sugarcane industry, with an area of more than 8 million hectares and an average yield of about 80 tons per hectare. According to the governmental statistics, 533 million tons were produced in 2011/2012. From fermentation of sucrose, sugar (9.34 million of tons) and bio-fuels (22.5 billion of liters of ethanol) were produced. Bagasse generated in the plants - 240 to 315 kg per sugarcane ton [1], after grinding the sugarcane, is burned to produce energy. The surplus is sold to electric companies, helping to ensure that the Brazilian energy matrix is one of the greenest on the planet. As a by-product of the combustion of sugarcane bagasse ashes generated in this process have been also investigated aiming to evaluate their characteristics as pozzolanic filler for the partial replacement of ordinary Portland cement (OPC). However, especially in the state of São Paulo, current regulations banned the burning of sugarcane straw before making manual harvesting of sugarcane, such as contributing to the development of mechanized harvesting. As a result of this advancement in environmental aspects, about 5% of the total mass of sugarcane remains in the soil, resulting in waste of the order of 20 tons per hectare.

Besides the possibility of using sugarcane bagasse and straw for the production of second generation ethanol (from cellulose), this biomass could also provide such properties that allow it to act as replacement of OPC. However, due to their chemical constitution rich in extractives, most crop residues have a strong chemical incompatibility with inorganic matrices.

The kinetics of hydration reactions in crop residues and OPC composites depends strongly on the characteristics of each constituent, and especially the effective interaction between them. The chemical composition of crop residues, particularly the content and nature of their extractives, is of fundamental importance for adequate binder's hydration reactions. Substances such sugars and complex salts can produce a film encapsulating the cement particles [2]. Depending on the degree of inhibition the binder's hydration reactions cannot occur.

In turn, the binder's chemical composition also interfere significantly in the hydration reactions, mainly in reaction kinetics and in the magnitude of the heat of hydration generated by these reactions. Among the constituents of cement, the concentration of calcium aluminate (C_3A) is one of major importance in the generation of heat of hydration, significantly speeding up the setting time of the binder. Then, in a lower rate, follows the tricalcium silicate (C_3S), and others cement's compounds (dicalcium silicate - C_2S, tetracalcium ferroaluminate - C_4AF) those do not contribute significantly to the generation of heat of hydration [2] and probably that will not be affected by chemical extractives of the crop residues in the initial setting period.

In general, neither crops residues nor wood processing wastes are chemically compatible with OPC. So, strategies aiming to minimize these inconveniences must be searched. Raw-material previously selected as residues from softwood processing, or then applying physical-chemical treatments to the wastes are the most effectives. A strategy, for example, is to employ catalyst, and among them, calcium chloride is one of the most effectives, by forming complexes with C_3A, thus accelerating the binder's hydration reactions [2].

OPC-crop residues interactions can be evaluated comparing the hydration curves of net cement paste and the composite ones. The main parameters evaluated are: the maximum hydration temperature, the time for its occurrence, the maximum rate of temperature rise versus time and also the comparison between the areas of each mixtures with the reference ones [3].

However, applying these parameters in the evaluation of the chemical compatibility between cement and crop residues it's necessary to consider that the mass ratio is one of the most important factor explaining the curve's behavior [4].

Moreover, despite the simple procedure to obtain the hydration curve parameters it must be taken in account that this technique allows only a necessary but not sufficient evidence to understand the real problem concerning residues and OPC interactions.

When compared with a conventional OPC-crop residue mixture, there are two main differences:

- Ratio cement to crop residues (in mass): for hydration curves, the ratio of 13.13 to 1; for commercial mixtures the ratio 2 - 3 to 1;
- Particle size: For hydration curves, particles that passed through the sieve opening # 200 (0.074 mm); for commercial mixtures, particles smaller than 4.8 mm.

The objective of this study was to evaluate the effect of several treatments applied to sugarcane straw particles, in order to minimize their chemical incompatibility with OPC.

Methodology

Residues from mechanized harvesting of sugarcane (straw and leaves) were obtained at Ester Mill, located at Cosmópolis, SP, at Brazil. Initially, residues were disintegrated, separating the fraction passing the 5.0 mm sieve opening, which was subsequently sent to the Polytechnic University of Valencia, at Spain. At the laboratory, sugarcane straw particles (SCSP) were disintegrated again, thus selecting the fraction passing the sieve opening of 0.315 mm.

Hydration curves of OPC paste (control) and several SCSP based mixtures were obtained. SCSP were employed in its natural condition (without treatment) and after being subjected to the physical or chemical treatments, aiming to reduce the extractives content and minimizing theirs inconvenient on the OPC setting.

The follow treatments were applied to SCSP:

- Natural: material in its original condition (NAT);
- Catalyst: calcium chloride (NCC), aluminum sulfate (NSA) and sodium silicate (NSS), in anhydrous condition, were separately dissolved in mixing water. Mass of anhydrous catalyst was 3% to the cement mass;
- Wash-up in warm water for 2 hours at 80 °C (LAV);

- Wash-up in alkaline solutions or suspensions: sodium hydroxide (SOD), sodium silicate (SIL), hydrated lime (CAL) and Portland cement (CEM) at 5% concentration;

- Mineralization: SCSP was soaked in sodium silicate solutions (2, 4, 5 and 6%) during 5 minutes, followed by: a) soaking in aluminum sulfate solution (10 and 15%); or b) soaking in a calcium chloride solution (10%), during 10 minutes [5]. Treatments were named SI*n*SA*m* or SI*n*CC*m* where *n* and *m* are the percentages of sodium silicate and the aluminum sulfate or calcium chloride solutions, respectively. After the mineralization, SCSP were dried before the mixture with OPC. Another possibility studied was also the mixture of OPC with SCSP immediately after the mineralization treatment, without drying SCSP.

Cement slurry of 200 g of cement and 50 g water was considered as a reference curve. For the composites 15 g of anhydrous SCSP was added to the cement, increasing water amount to 80 g. Cement was initially mixed with the residue in a plastic bag and then it was added the mixing water, with catalysts in some treatments. However, it was observed that, when using SCSP mineralized and previously dried, there was a strong and rapid exothermic reaction, which eventually impairing the workability of the mixture.

The methodology of hydration curve analysis was proposed by [3] and it was employed in this research work to assess the chemical compatibility between SCSP and OPC. The maximum temperature of hydration and the time required for its occurrence were evaluated.

Mixtures were placed in a polystyrene box in a pseudo adiabatic condition. Then thermocouples type K was putted into four mixtures for each evaluation. Test was controlled by a HI-92804C device. Temperature was recorded at every 10 minutes, during 24 hours. Maximum temperature and the time for its occurrence were compared to those of the neat cement paste.

Results and Discussion

The aim of this research work was to search, in a quick way, an effective treatment to be applied to the SCSP. Fig. 1 depicted some temperature evolution curves of mixtures of SCSP with cement using different catalysts. As expected (Fig. 1), by its extractives content, natural SCSP (NAT) was strongly inhibitory to the cement setting. For all of the evaluated curves, peaks were only observed at initial setting of the binder. However, as observed mainly for NSS and NCC, theses peaks did not correspond to the normal cement setting (6-10 h), but they can be attributed to the initial reactions of the extractives with some of the cement compounds, mainly C_3A. This behavior is explained by NSS curve that shows clearly two peaks at different setting times.

SCSP remained non compatible with OPC paste even after submitted to the physical (LAV) and chemical treatments (NSS, NCC and NSA) (Fig. 1). As consequence, the maximum of temperature was only 32 °C for NSA; the time for its occurrence was about 11 h. In comparison, cement paste showed a maximum temperature of 50 °C after 8.33 h.

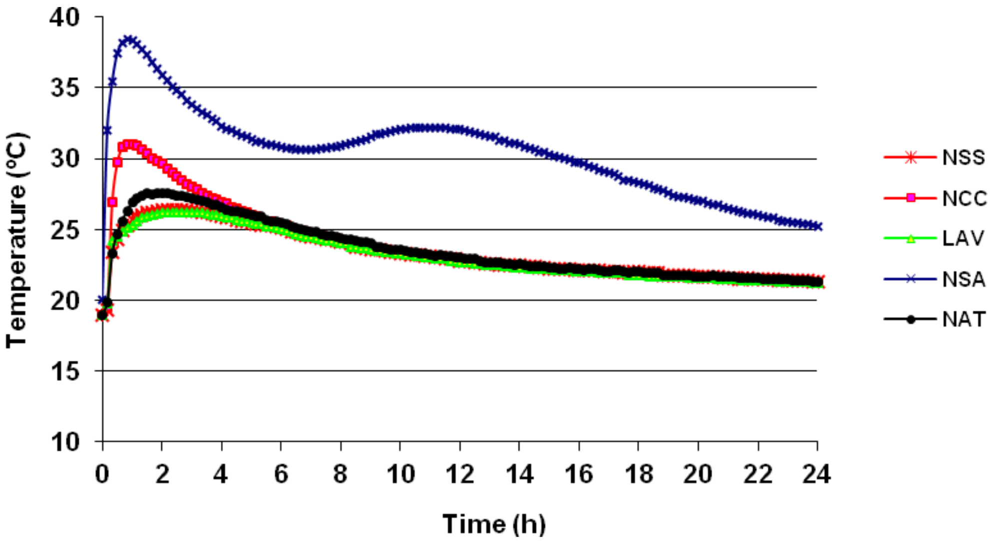

Figure 1. Hydration curves for natural SCSP and catalysts application on SCSP/cement mixtures. NAT = in nature material; NSS = natural + sodium silicate at 3%; NCC = natural + calcium chloride at 3%; NSA = natural + aluminum sulfate at 3%; LAV = wash-up in warm water (2 h at 80 °C).

Cement paste is strongly alkaline and the pore water at the interface region can attack SCSP provoking its lack of adhesion with the binder. On the other hand, extractives from SCSP can migrate to the particle's surface inhibiting cement setting. Extractive content from SCSP was very high and none of the alkaline solutions was effective enough to overcome this drawbacks. Only SCSP treated in a sodium hydroxide solution (SOD) shows a tendency similar to those of the cement paste (Fig. 2). However, maximum temperature was only about 29.3 °C and cement setting was about 13 h. The same time necessary to the cement setting was observed for the others alkaline treatments. But maximum temperature remains almost the same of the environment denoting that binder reactions were completely stopped by extractives action.

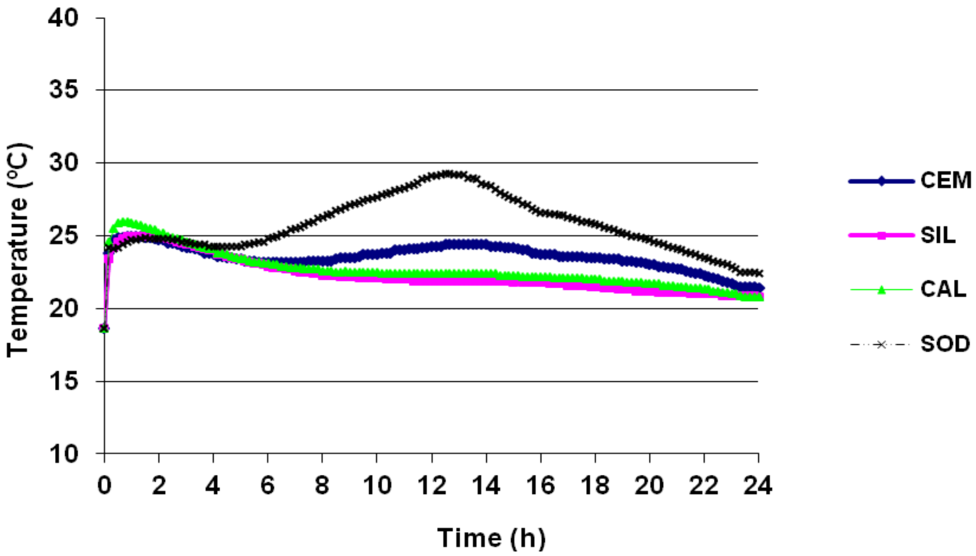

Figure 2. Hydration curves for mistures of cement and SCSP with alkaline treatments. SOD = sodium hydroxide solution in 5%; CAL = hydrated lime suspension in 5%; SIL = sodium silicate solution in 5%; CEM = Portland cement suspension in 5%.

Mineralization treatment was applied to the wood aiming to enhance its performance against fire and fungi [5] and also it was applied to the sugarcane bagasse aiming to modify its behavior with the cement paste [6].

Mineralization is produced by a double effect of the sodium silicate when combined in a water solution with aluminum sulfate or calcium chloride. These soluble salts react and produce an insoluble one (aluminum-sodium silicate or calcium-sodium silicate) encapsulating SCSP and preventing the migration of the extractives to the SCSP surface. At the same time, these complex salts can perform as a super catalyst overcoming the deleterious effects of the SCSP. Inorganic substances as aluminum silicate or calcium silicate were deposited in the wood cells improving its resistance against fire and decay [5].

Mineralization performance depends on the compounds contents. For sodium silicate (5%) and aluminum sulfate (10%) the reactions when mineralized SCSP were mixed with cement are very fast and the temperature peak occurs in a few minutes (Fig. 3, SI5SA10 curve). This fact is an inconvenient for the preparation of the SCSP-cement composite because this open time difficult the composite manufacturing. For the same contents, but replacing aluminum sulfate by calcium chloride (Fig. 3, SI5CC10 curve), the peak (6.25 h, 49 ºC) is near of those of the cement paste denoting that this treatment is an alternative that allows employing SCSP as an alternative aggregate for cement composite manufacturing.

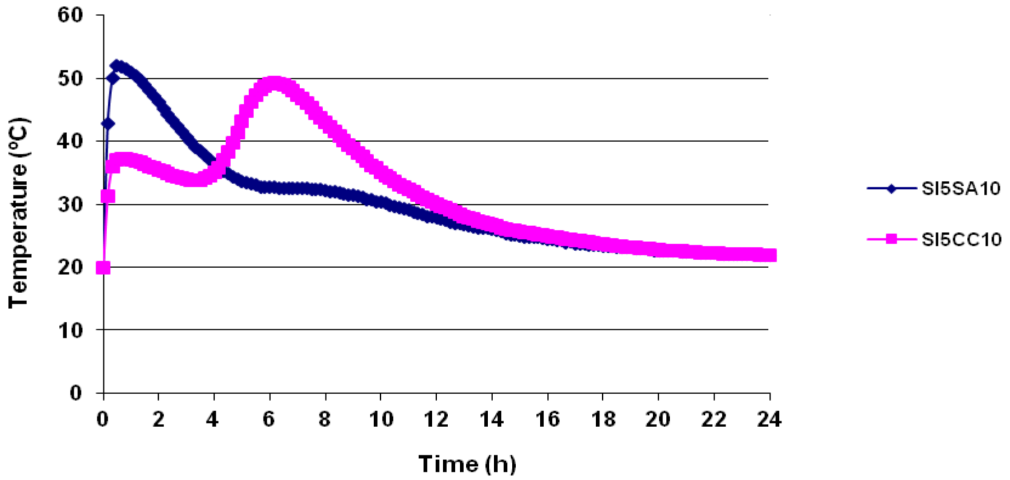

Figure 3. Effect of SCSP mineralization (dry mixture) on temperature evolution.
SI5SA10: 5% sodium silicate + 10% aluminum sulfate
SI5CC10: 5% sodium silicate + 10% calcium chloride

Figure 4 shows the hydration curves of mineralized SCSP, mixed without previous drying, i.e. immediately after the treatment. In this case, some mixtures for mineralizing SCSP were tested using aluminum sulfate (SA - 10 and 15%) with sodium silicate (SI - 2, 4 and 6%). Except for the combination of 15% of aluminum sulfate, with 4% of sodium silicate (SI4SA15), all of the hydration curves showed proper behavior denoting that sodium silicate (2, 4 or 6%) and aluminum sulfate (10%) combinations showed kinetic behavior similar to those of the cement paste (slight reduction in time for highest reached temperature). According to the hydration curves features, the solution of sodium silicate at 4% and aluminum sulfate at 10% can be considered as the most effective to be applied to the SCSP (peak: 4.5 h, 48 ºC).

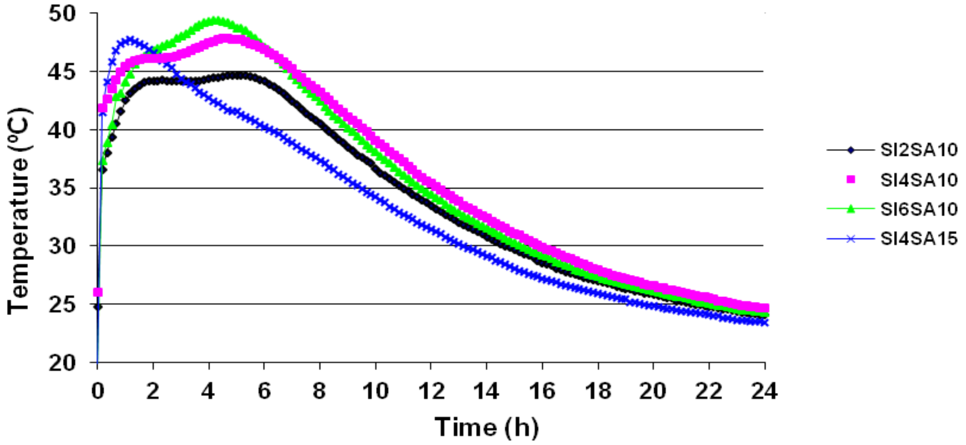

Figure 4. Effect of SCSP mineralization (wet mixture) on temperature evolution.
SI2SA10: 2% sodium silicate + 10% aluminum sulfate;
SI4SA10: 4% sodium silicate + 10% aluminum sulfate;
SI6SA10: 6% sodium silicate + 10% aluminum sulfate;
SI4SA15: 4% sodium silicate + 15% aluminum sulfate

4. Conclusions

Sugarcane straw particles (SCSP) in its natural condition showed great chemical incompatibility with OPC. Several treatments applied to the SCSP were not successful to improve its behavior in cement composites. Among the treatments applied to the SCSP only the mineralization was interesting for overcoming the drawbacks produced by extractives on cement setting. SCSP treated by soaking in sodium silicate solution at 4%, followed by a second soaking in aluminum sulfate at 10%, permitted an appropriate cement setting process.

5. Literature References

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